PROOF BY LOWER BOUND METHODS THAT

NO SINGLY-EXCITED BOUND STATES EXIST IN H^-*

by

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Variational calculations for the lowest ^1S state in the hydrogen negative ion, H^-, showed[1] quite early that this state is bound. However, similar calculations[2,3,4,5] for the lowest ^3S state, the first excited ^1S state, and the lowest ungerade ^3P state have never produced an upper bound below the onset of the one-electron continuum. It has therefore been assumed that there are no singly-excited bound states in H^-. If calculated lower bounds for these states could be obtained and were found to lie above the onset of the continuum (-0.50 a.u. for these states), this would conclusively prove that these states cannot be bound.

The standard available lower bound methods, however, are not able to produce lower bounds above the beginning of the continuum. It is clear that the Temple[6] and Weinstein[7] methods do not apply here. Also, the methods of Bazley and Fox[8], and the modification due to Gay[9], cannot be applied because they require that the lower bound calculated from an ℓ^{th} order secular determinant be below $E^o_{\ell+1}$, the $\ell+1^{st}$ unperturbed eigenvalue. In H^- all these unperturbed eigenvalues $E^o_{\ell+1}$ lie <u>below</u> the onset of the one-electron continuum, so these methods can never produce a rigorous lower bound that lies <u>above</u> the beginning of this continuum.

We have recently been able to extend a lower bound procedure[10] that we presented earlier. As originally presented, our procedure is also limited to lower bounds lying below $E^{o}_{\ell+1}$; but we have now obtained a criterion that justifies the use of roots of the secular determinant above $E^{o}_{\ell+1}$ as rigorous lower bounds. In effect this criterion determines whether a given root of the determinant will increase or decrease if the order of the determinant is increased. We then reason as follows: if a state K is bound (i.e., its energy E_K is below -0.50 a.u.), then for some determinant sufficiently large, say LxL, it will be true that E^{L}_{K}[11] $< E^{o}_{L+1}$, and therefore E^{L}_{K} is a rigorous lower bound to E_K. However, if the $K^{\underline{th}}$ root of the determinant has only increased as the order of the determinant has been increased, then E^{ℓ}_{K} for the smaller $\ell x \ell$ determinant is also a lower bound to E_K -- even if $E^{\ell}_{K} > E^{o}_{\ell+1}$. We shall present the details justifying this extension of our lower bound method in a later publication.

The lower bounds we have obtained for H^- are presented in Table I. The number ℓ given with the lower bound is the order of secular determinant used in each case. Note that even for the $1s^2$ state the "lower bounds" cannot at first glance be claimed as rigorous lower bounds since they are above $E^{o}_{\ell+1}$. The criterion that we have developed, however, reveals that these roots must increase as the order of the determinant is increased, and they are therefore rigorous lower bounds.

We wish to emphasize that we are <u>not</u> claiming that there is a bound 1s2s ^3S state in the one-electron continuum. The calculation says that the lowest bound ^3S state must lie above -0.4871 -- and since there can

be no ^3S bound states above -0.50, no ^3S bound states exist. In light of the work of O'Malley and Geltman[12] it seems clear that this numerical value is related to a resonance in the electron scattering off H atoms. However, the resonance will occur at such low energy (a few tenths of an ev) that it is doubtful that it can be observed experimentally.

Our calculations give lower bounds for the 1s2s ^1S and 1s2p ^3P states that are above the lower bound for 1s2s ^3S, and therefore these states are also not bound.

Another excited state of some interest is $2p^2$ ^3P; it is the lowest even parity ^3P state and is bound in the He atom. The one-electron continuum for states of this symmetry begins at -0.1250 in H^-. E. Holøien has obtained[3] an upper bound of -0.1243, but we caution that though this is close to -0.1250, it does not necessarily indicate that the state is "almost" bound. In fact, if a state is not bound, an unrestricted variational calculation will always converge to the onset of the continuum if a sufficiently flexible trial function is employed.[2,4] However, the best (highest) lower bound that we have been able to obtain is -0.1260 (with an ℓ=5 order determinant). We can only conclude from this that it is possible that $2p^2$ ^3P is bound in H^-. To prove that it is bound requires an upper bound that is below -0.1250.

The author is happy to acknowledge his many helpful discussions with Professor E. Bright Wilson, Jr., concerning this problem.

TABLE I. Lower Bounds for H^- (atomic units, 1 a.u. = 27.2 ev)

State	Upper Bound	Lower Bound (ℓ)	$E^{\circ}_{\ell+1}$	Difference
$1s^2\ ^1S$	-0.5278	-0.5623 (1)	-0.6250	0.0345
$1s^2\ ^1S$	-0.5278	-0.5536 (2)	-0.5556	0.0258
$1s2s\ ^3S$	--	-0.4871 (1)	-0.5556	--

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†NSF Predoctoral Fellow.

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A previously presented lower bound method has been extended to make it possible to obtain lower bounds above the beginning of the one-electron continuum in a two-electron atom. The nature of this extension is briefly predicted and the method is applied to the eigenvalues of the hydrogen negative ion, H^-. It is found that the lowest bound ^3S state must lie above -0.4871 a.u. -- and since there can be no bound states of this symmetry above -0.50 a.u. there are no bound ^3S states in H^-. Also the lowest ^3P_u (1s2p) state and the first excited ^1S (1s2s) state have lower bounds above -0.50 a.u.

The one-electron continuum for ^3P_g states begins at -0.125 a.u. in H^-. The best lower bound obtained for the lowest state of this symmetry($2p^2$) is -0.1260. Thus we cannot conclude that $2p^2$ ^3P is not bound.

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